

MOLECULAR TRANSPORT AND FLUIDICS IN CARBON NANOTUBE

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In this article we review recent developments in molecular transport and fluidics in carbon nanotube (CNT)-based nanochannels. Atomic molecular dynamics simulations and theoretical studies based on Fokker–Planck diffusion equation on the transport of large and long polymer molecules in CNTs are the focus of the article. Fast translocation and diffusion processes of large molecules in CNTs are reviewed and discussed, considering the effects of interfacial interactions and molecular conformations and structures at interface. The transport features for multiple molecules diffusing through CNTs are also discussed.

Keywords: Molecular transport; nanofluidics; carbon nanotube; nanopore; nanochannel.

1. Introduction

Molecular transport and fluidics in confined spaces are very different from regular fluidics behavior in the diffusivity features and in the roles of individual molecule structure and conformation. Nanochannels or nanopores exist in both fabricated materials and biological systems. Some examples for the former are zeolite materials,¹ solid state silicon-based nanopores,² and carbon nanotubes (CNTs),^{3–8} while the latter has examples such as nanopores in biological membranes.^{9,10} Atomic level interactions and interfacial structures are crucial for the transport properties in these nano-scaled channels. There are extensive ongoing theoretical and experimental efforts to investigate and to realize nanochannels/nanopore systems for their applications in molecular transportation and separation, molecular sieving, DNA sequencing, and drug delivery, etc.

Recently, theoretical and simulation studies have been pursued on numerous nanochannel or nanopore systems, such as nuclei acid (DNA/RNA) translocation through biological membranes^{9,10} or CNT-based nanochannels,^{11,12} gas,^{3,4} water,¹³ and long polyatomic molecules⁵ through CNTs. Among the proposed nanochannels, CNT-based systems have several advantages. The strong carbon–carbon bonds

on CNT surfaces make them structurally stable and mechanically strong. The radius of CNTs vary from several angstroms to tens of nanometers, depending on whether they are single-wall, multiwalled, nanocone or bamboo structured. Experiments and theoretical studies have shown that the electronic transport properties of CNTs are very sensitive to surrounding environment and CNTs are good sensors to gas and biological molecules.^{14,15} The good functionalization ability of CNTs from both inside and outside with doping or (chemical or physical) adsorptions¹⁶ can add extra chemical and fluid sensing¹⁷ and detecting features to CNT nanochannel systems towards their applications in molecular separation/sieving and DNA sequencing, etc. The understanding of molecular transports and nanofluidics inside CNTs thus are not only fundamentally important but also crucial for their applications as nanochannel-based devices. In this article, we review recent developments in the field of transportations of large molecules from theoretical point of view. Recent experimental progresses are also briefly discussed.

2. Interaction and Structure at Molecule–Carbon Nanotube Interface

2.1. *Interfacial interaction*

The interfacial interactions between molecules and CNT walls are crucial for the structures and conformations of the molecules, as well as for determining the transport and diffusion properties of the molecules inside CNT channels. The interactions between a molecule and CNT range from chemical interactions with strong bonding to physical interactions such as van der Waals (VDW) interactions. The electrostatic interactions are usually less significant due to the negligible free or induced charges on CNT surfaces. These can become important when doping or chemical functionalization is applied to the CNTs. While hydrophobic interactions are also important in water solvent systems,¹³ VDW interactions have been shown to play a dominant role in molecular transportation inside CNTs. For a polyethylene (PE) molecule, the attractive VDW interaction energy is up to 0.1 eV per unit.⁵ The high curvature of CNTs in small radii tubes induces larger VDW attractive interaction energies, which always have higher values inside CNTs than outside. For polymer or protein molecules with larger subgroups, the VDW interaction energy can be larger than that of simple PE molecules. For example, a homogenous single strand DNA oligonucleotide molecule was found to have VDW interaction energy of about 0.35 eV per base with CNT walls.¹¹ The VDW interaction plays an important role not only in determining the conformation of a molecule inside CNTs but also in the transport properties, which to be discussed later.

2.2. *Conformation and structure at carbon nanotube interface*

The attractive VDW interaction energy between a molecule and CNT, excluding the loss of interaction energies with solvent molecules outside the CNT, usually provides

an energetically favorable force for the molecule to be included into the CNT. At the same time, the decrease of the entropy of the molecule in the confined space by the CNT presents a competing force against the inclusion. The entropy effect is especially important and complicated for large and long polymer and protein molecules. The entropy of a long polymer molecule is dependent on the conformation Ω of the molecule as $S = k_B \ln \Omega$, where k_B is the Boltzmann constant. According to scaling law, the conformation $\Omega \sim N^{\xi-1} q_{\text{eff}}^N$, where N is the number of monomer units in the molecule; q_{eff} is the effective coordination number for each unit; and ξ is a scaling parameter, which has value of 1 for rigid polymer model, 1.5 for random walk of free freight model, and $(1 + 1/7)$ for self-voided random walk model.¹⁸ The entropy of a polymer molecule therefore can be expressed as:

$$S = k_B \ln \Omega = k_B(\xi - 1) \ln N + k_B N \ln q_{\text{eff}} + \text{const}. \quad (1)$$

When a molecule goes inside a CNT, both ξ and q_{eff} decreases due to the confinement in the radial direction. While a totally rigid molecule has q_{eff} and $\xi = 1$, molecules inside a CNT can still have a few degrees of freedom to distribute along the surface of the CNT. From equilibrium MD simulations, it has been found that PE molecules choose to be at the CNT wall with an equilibrium distance of VDW interactions, and that they are usually curved around the surface of the CNT.⁵ Figure 1 shows the radial distribution function (RDF) of PE molecules confined in a CNT (10, 10) at the equilibrium temperature of 600 K, for cases of $N = 5, 20,$ and 40, respectively, where N is the number of monomer units in the polymers. An adsorption peak around 3.75 \AA from the CNT wall is observed in all cases. It can be seen that the distribution of the RDF is much broader from the right side (large

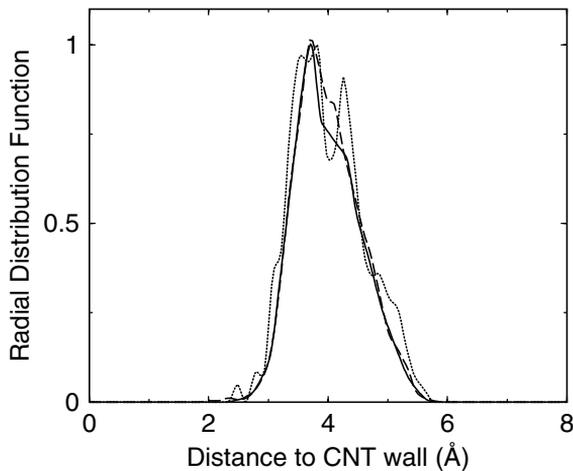


Fig. 1. The radial distribution function (RDF) of N -unit polyethylene molecules inside a CNT (10, 10) from equilibrium MD simulations at $T = 600 \text{ K}$. The dotted, dashed, and solid lines are for $N = 5, 20,$ and 40 units, respectively.

distance region) of the peak than that from the left side (small distance region). A shoulder in the RDF has been formed adjoined to the adsorption peak in the cases of $N = 20$ and 40 , which is further shown as a secondary peak in the case of $N = 5$. This indicates that the molecules try to choose conformations with more freedoms. Similar conformations have also been observed in protein molecules (DNA/RNA) confined in CNTs.^{11,12} The competing factors of minimizing interaction energy and maximizing entropy are expected to have more interesting effects in short CNT channels.

Ordered structures of polymer molecules have been found at the interface of CNT walls, both outside and inside, where discrete adsorption layers of molecules have been observed in atomic level MD simulations.¹⁹ Such ordered structures have also been reported in the case of water molecules confined in CNTs.²⁰ The presence of extra hydrogen bonds together with the VDW interactions with the tube walls induces water molecules to form chained and shelled structures.²⁰

3. Molecular Transport in Carbon Nanotube

3.1. Fokker–Planck equation for translocation process

Both the equilibrium and dynamic (transport) properties of large and long polymer molecules in CNT channels depend on the combined factors of the molecular interaction energy and entropy at finite temperatures. The free energy of a system is defined as $f = E - TS$. In a general case, an N -unit (polymer) molecule would be partly inside (n units) and partly outside ($N - n$ units) of a CNT. The free energy for such a system can be expressed as following, taking into account of the entropy as in Eq. (1):

$$\begin{aligned}
 f(n) &= f_1 + f_2 \\
 &= e_1 \times (N - n) + e_2 \times n - k_B T (\xi_1 - 1) \ln(N - n) - k_B T (N - n) \ln q_1 \\
 &\quad - k_B T (\xi_2 - 1) \ln n - k_B T n \ln q_2 + \text{const.} \\
 &= k_B T \left[n \times \left(\frac{\Delta\mu}{k_B T} + \ln \frac{q_2}{q_1} \right) - (\xi_1 - 1) \ln(N - n) - (\xi_2 - 1) \ln n \right] + \text{const.}
 \end{aligned}
 \tag{2}$$

The suffixes 1 and 2 are for the portion of the polymer outside and inside of the CNT, respectively and we will use this label throughout the article. The difference of energy per unit $\Delta\mu = e_2 - e_1$, between the two configurations with polymer inside/outside CNT, is referred to as the difference in chemical potential. The height and shape of possible energy barriers from exclusion to inclusion of polymers into CNTs depend on the values of the parameters of $\Delta\mu$, ξ and q .^{21,22}

The molecular transport inside CNT has two processes: translocation and diffusion. The translocation of a polymer molecule into a CNT (possibly surrounded by polymer or water solution) is a thermodynamics process and the equation of motions can be described by Langevin equation, $m dv/dt = -m\gamma v + \mathbf{R}(t) + \mathbf{F}$,

where $-m\gamma\mathbf{v}$ is the friction force (γ is the friction coefficient), $\mathbf{R}(t)$ is the random stochastic force from the Brownian motion of surrounding molecules, and \mathbf{F} is the systematic force from external potentials, which can be from the chemical potential mentioned in Eq. (2). The solution to the above Langevin equation is a statistical one because of the presence of random stochastic forces.

As to the problem we are interested in here, a statistical translocation time for a polymer molecule through a CNT channel can be obtained using Fokker–Planck equation. The probability function, $P(n, t)$, with n segments of the polymer molecule into the CNT at time t is described by a one-viable Fokker–Planck equation, $\partial P(n, t)/\partial t = \tilde{L}P(n, t)$, where \tilde{L} is the Laplace operator.²³ The mean first translocation time τ of a N -unit polymer molecule into a CNT channel can be expressed as following (assuming only the head unit of the molecule is inside the CNT at $t = 0$) (also see Appendix)⁵:

$$\tau = l_0^2 \int_1^{N-1} e^{f(n)/k_B T} dn \int_1^n \frac{1}{D(n', N-n')} e^{-f(n')/k_B T} dn', \quad (3)$$

where l_0 is the length of a single unit; $f(n)$ is the free energy as expressed in Eq. (2); $D(n, N-n)$ is the diffusion coefficient for the molecule with $n/(N-n)$ units inside/outside the CNT channel. According to scaling law, the general form of $D(n, N-n)$ is expressed as follows:

$$\frac{1}{D(n, N-n)} = \frac{(N-n)^{\nu_1}}{D_1} + \frac{n^{\nu_2}}{D_2}, \quad (4)$$

where D_1 and D_2 are the diffusion coefficients for a single monomer outside and inside CNT, respectively, and ν_i is an exponential coefficient constant, which has a value of 0.5 in Zimm model, 1 in Rouse model, or 0 if only local friction at the ends of the CNT channel is considered.²⁴ The mean first translocation time τ can be obtained by applying Eqs. (2) and (4) into Eq. (3). As it can be seen, τ is a function of $\Delta\mu$, q_i , γ_i , ν_i ($i = 1, 2$), and its value increases with larger ν_1 , ν_2 , γ_1 and decreases with a larger γ_2 . For the case of large N , the mean first translocation time can be expressed as the following:

$$\tau(\nu_i, \gamma_i) = \frac{b^2}{|(V\mu/k_B T) + \ln(q_2/q_1)|} \left[\frac{N^{\nu_1+1}}{(\nu_1+1)D_1} + \frac{N^{\nu_2+1}}{(\nu_2+1)D_2} \right] + o\{(\gamma_i - 1)N^{\nu_i}\}, \quad (5)$$

assuming that $N|V\mu/k_B T| \gg 1$ and $V\mu < 0$ (which is the case of interests here). The contributions dependent on γ_i , as shown in the second term of Eq. (5), are scaled an order of magnitude smaller as compared with the first term for cases of large N , and has less influence on τ . The diffusion properties described by D_i and ν_i largely determine τ . Due to the one-dimensional confinement by the CNT channel ν_2 is larger than ν_1 , which thus has a larger influence on τ for large N . The diffusivity of polymer molecules suggests that $\nu_2 \sim 1$, indicating $\tau \sim N^2$.⁵ The diffusion properties of large molecules will be further discussed later.

The Fokker–Planck equation has also been used to understand the translocation of a protein molecule through zero or very short length pores to mimic the biological nanopores in membranes.^{21,22} In such cases, local or uniform frictions and position-independent diffusion coefficients are usually introduced, and the diffusion of molecules in channels or pores is omitted. The diffusion properties inside nanotubes however dominate in cases of CNT channels with a comparable or longer length to that of molecules, as shown in Eq. (5). This is due to the limited conformation space for the molecules, which induces a higher ν inside CNTs than outside. The translocation time of a molecule is directly dependent on the change of chemical potentials for the molecule from outside to inside a nanotube channel. Simulations on water and DNA molecules have shown that moderate changes in VDW interaction strength can largely affect the translocation process in CNTs.^{12,13} The chemical potential can be modified and controlled by external fields, such as electric field in the case of DNA/RNA translocation through membranes. Chemical functionalization at CNT walls can also provide more controllable external potentials to the system. More experiment and theoretical studies are obviously needed to understand further on these issues.

3.2. *Molecular simulations for translocation process*

Recently, MD simulations with Langevin equation have been conducted on the translocation of PE molecules into CNTs.⁵ The diffusion of polymer molecules is assumed within Zimm model in solutions outside CNTs, in which $D = k_{\text{B}}T/(M\gamma) \sim N^{-0.5}$ (N is the number of units and M is the total mass of a molecule). Thus, the friction coefficient $\gamma = \gamma_0 N^{-0.5}$, where γ_0 is the friction coefficient for a monomer. The random force $\mathbf{R}(t)$ is assumed to be white noise, obeying the fluctuation–dissipation theorem. Figure 2 shows the motion of the head unit of a 40-unit PE molecule in a solution with three different friction coefficients, and the molecule is just outside a 15 Å long CNT (10, 10) at $t = 0$. The carbon atoms on the CNT were modeled explicitly and were kept fixed during the simulations. It can be seen that for $\gamma_0 = 50 \text{ ps}^{-1}$ (solid curve, representing decane solution), the PE molecule begins to go into the CNT at 500 ps, and reaches the other end of the CNT at about 750 ps. Then, the head unit of the molecule wanders inside and outside the CNT because of the attractive VDW interactions. The time for the inclusion into the CNT is increased with larger friction forces from the surrounding solution. The data present in Fig. 2 is from a single trajectory. Figure 3 shows the snapshots of the PE molecule into the CNT at $t = 0, 600,$ and 750 ps, for case of $\gamma_0 = 50 \text{ ps}^{-1}$. The side views show that the molecule curved around the CNT wall to minimize the interfacial interaction energy. Similar conformations were also observed for DNA/RNA translocation through CNT in MD simulations.^{11,12}

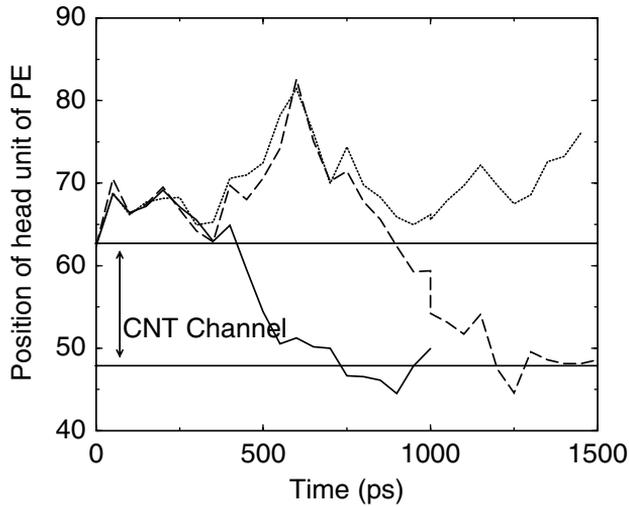


Fig. 2. The position (along the nanotube axis direction) of the head unit of a 40-unit polyethylene molecule as a function of time during its translocation into a 15-Å long CNT (10, 10). The data is of a single trajectory from equilibrium MD simulations at $T = 600$ K. The solid, dashed, and dotted lines are for the friction coefficient $\gamma_0 = 50, 75, 100 \text{ ps}^{-1}$, respectively, in Langevin equation. The position of the CNT channel is marked in the figure.

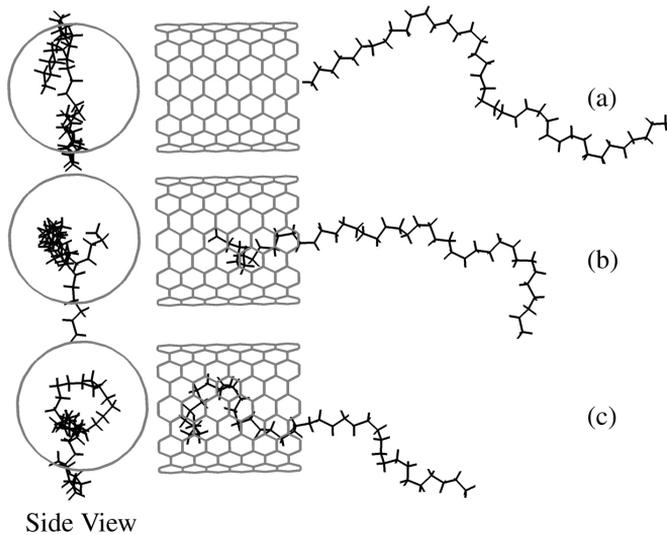


Fig. 3. The snapshots of a 40-unit polyethylene molecule transporting into a 15-Å long CNT (10, 10), from equilibrium molecular dynamics simulations with $\gamma_0 = 50 \text{ ps}^{-1}$ at $T = 600$ K. (a) $t = 0$ ps, the molecule is just outside the CNT; (b) $t = 600$ ps, the molecule is partially inside the CNT; and (c) $t = 750$ ps, the molecule reaches the other end of the CNT.

4. Molecular Diffusion and Fluidics in Carbon Nanotube

Molecular diffusions take place after the translocation of a molecule into a CNT channel. This process is largely different from a macroscopic flow, where nonslip conditions at walls are usually assumed. In a confined space as small as within a CNT, the dimension of the tube is comparable with that of molecules especially large molecules. The interfacial behavior at the CNT surface thus dominates the diffusion and the fluidics of the molecules. Simulation studies on water and small hydrocarbon molecules showed very fast diffusion,^{3,4,13} which is attributed to the smoothness of CNT walls. Large slip lengths and small Maxwell friction coefficients were found at CNT surfaces in a previous theoretical study.²⁵

The diffusion of larger molecules such as long polymer or nuclei acid molecules is more complicated due to the entropy effects. Molecular conformation and connectivity in these cases play important roles in the transport and fluidics inside a CNT channel. Molecules confined in a CNT collide with the channel wall frequently and reach their thermal equilibrium with the wall even when they are not directly connected to any outside heat bath. The velocity distribution of confined PE molecules is found obeying Maxwell distribution function $e^{-mv^2/2k_B T}$ from equilibrium MD simulations. Thermodynamic relations are therefore expected to be obeyed in such systems.

The self-diffusion of a confined molecule gives direct information on the effect of interfacial interactions and thermal collisions with CNT walls. The self-diffusion coefficient D_{\parallel} along the CNT axis can be calculated by either following the displacement of the position of the center mass of the molecule as a function of time as:

$$D_{\parallel} = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle [r_{\parallel}(t+t_0) - r_{\parallel}(t_0)]^2 \rangle, \quad (6)$$

or by integration of the autocorrelation function of the velocity of the center mass of the molecule.

Figure 4 shows the mean square displacement (MSD) of the center mass of a 40-unit PE molecule as a function of time in a (10, 10) CNT at $T = 600$ K, from MD simulations.⁵ For a short time period ($t < 40$ ps), ballistic transport of the molecule is observed with $\partial \log(MSD)/\partial \log t \sim 2$. Such feature has also been observed in a separated simulation of decane molecule imbibitions in CNTs with capillary lengths scaling as t^2 .²⁶ After long period, the thermal collisions with the CNT wall diminish the memory of the initial velocity and the molecule begins to behave diffusively. As shown in Fig. 4, the slope ~ 1 of $\log(MSD)$ versus $\log t$ suggests Fick's law is obeyed for $t > 40$ ps. The autocorrelation function $C_{vv}(t)$ of the velocity of the center mass of the PE molecule is shown in the inset in Fig. 4. A critical time of $t = 40$ ps is observed beyond which C_{vv} approaches zero. Using the definition in Eq. (6), the self-diffusion coefficient constant D_{\parallel} is found to be $25.4 \pm 0.5 \text{ \AA}^2/\text{ps}$ for the 40-unit PE molecule diffusing inside the (10, 10) CNT at $T = 600$ K and zero pressure. An extrapolated value of $D_{\parallel} \sim 10^3 \text{ \AA}^2/\text{ps}$ is obtained for methane gas

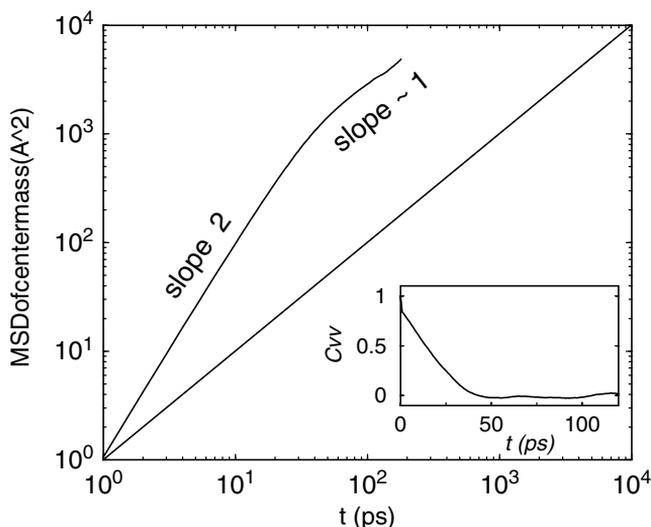


Fig. 4. The MSD of the center mass of a 40-unit polyethylene molecule diffusing inside a CNT (10, 10) as a function of time in log-log scale. At $0 \text{ ps} < t < 30 \text{ ps}$, the slope of $\log(\text{MSD})$ versus $\log t \sim 2$; at $t > 40 \text{ ps}$, the slope ~ 1 . Inset: The velocity autocorrelation function C_{vv} as a function of time. The data is averaged over 12 sample sets.

molecules at $T = 300 \text{ K}$, using a modified Einstein relation, $D_{\parallel} = k_{\text{B}}T/Nm_0\gamma_{\text{eff}}$, where γ_{eff} and m_0 is the effective friction coefficient and the mass of a monomer in an N -unit polymer molecule, respectively. Small friction with $\gamma_{\text{eff}} \sim 10^{-2} \text{ ps}^{-1}$ is found for the PE molecules inside CNT. The diffusion of the polymer molecules are found to be much faster in CNTs as compared with in silicate zeolite systems.⁵ Direct MD simulations of methane gas molecules in CNTs also showed such fast diffusion feature, with $D_{\parallel} \sim 10^4 \text{ \AA}^2/\text{ps}$ for the same conditions, without including the thermal fluctuations of CNT walls.³ For short polymer molecules with small N , the Einstein's relation is expected to need further modifications as the confining effect on the conformation is less significant as compared with for long molecules. This could also contribute to the difference between the extrapolated value of D_{\parallel} and the value from the direct MD simulations for methane molecules.

The diffusion of an N -unit polymer molecule is expected to decrease with increase of the number of monomers in the molecule. Figure 5 shows the velocity autocorrelation functions for $N = 5, 20$, and 40-unit PE molecule diffusing in a CNT (10, 10) at $T = 600 \text{ K}$. It can be seen that a longer molecule has a shorter critical time for ballistic transport and a smaller diffusion coefficient due to the larger contact area with the thermally fluctuating tube walls.

The diffusion properties of small gas molecules at various pressures have also been studied through MD simulations recently. Both the transport and the self-diffusivities of H_2 and CH_4 gas molecules have been found to be much faster in

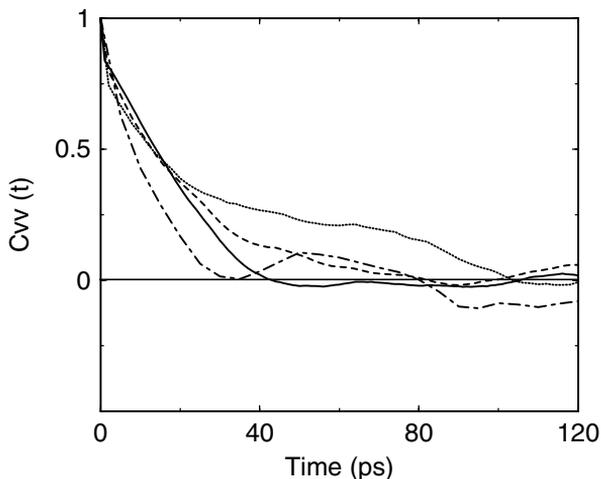


Fig. 5. The velocity autocorrelation function of N -unit polyethylene molecules in CNT (10,10) at $T = 600$ K. The dotted, dashed, and solid lines are for cases of a single molecule with $N = 5$, 20, and 40, respectively. The dash-dotted line is for the case of two molecule diffusion in the nanotube with $N = 20$. The data is averaged over eight sample sets.

CNTs than in silicalite or ZSM-12 zeolite at pressures of up to 100 bar in these studies.³ The transport diffusivities of the gas molecules have been found to be almost constant with increasing pressures up to 100 bar, while the self-diffusivities drop with applying pressures and reach stable values at high pressures.

A general relation $\langle [r_{\parallel}(t+t_0) - r_{\parallel}(t_0)]^2 \rangle / 2t = 2Dt^n$ can be expressed for the diffusion properties of fluids, where $n = 1$ is for normal diffusions obeying Fick's law. The diffusion of small molecules such as H_2 and CH_4 or diluted large molecules have been found to obey Fick's law in CNTs.^{3,5} For large molecules at high densities, the collective motions of multiple molecules are expected as the molecules cannot pass each other easily in the nanometer size channels. In cases of thermally fluctuating walls single file transports of molecules with $n = 1/2$ in above expression are expected.²⁷ Transition transport behavior, which is between Fickian behaviors and single file transports, with $0.5 < n < 1$, have been observed in recent MD simulations for ethane and ethylene molecules. The MD simulations have also suggested that such transport feature would convert to normal Fickian diffusion at long time.⁴ For multiple large molecules, single file transport diffusions are expected, while the collision processes between molecules can be more complicated as compared with that in simple models. In a simple hard sphere model, when two molecules collide, they simply exchange momentums.²⁷⁻²⁹ For large molecules with complicated compositions, the momentum exchange may happen only between the end units of the two colliding molecules. The impact of the exchange of momentums will further dissipate along the molecules; and the changes of conformation and velocity of the molecules are expected to be related to such dissipation processes. The

collision between molecules is expected to slow the diffusion as shown in Fig. 5 (dotted-dashed line) for two 20-unit PE molecules in a CNT (10, 10). A shorter ballistic region and smaller diffusion coefficient can be seen as compared with a single 20-unit PE molecule diffusion (dashed line in Fig. 5).

5. Discussion

Beside the theoretical and simulation studies reviewed here, important advancements have also been made in experiments. Recently one-dimensional channels such as multiwall carbon nanotubes embedded in polymer matrix,⁶ in silicon nitride membrane,⁷ and in crystalline urea-based structures⁸ have been fabricated. The transport and diffusion properties of ions, deuterated water molecules, and dibromooctane (DBO) and pentadecane (PD) molecules have been investigated experimentally in these nanochannels systems. The field of molecular transport in CNT channels is still in its initial stage and there are many important issues needed to be addressed such as the multiple molecular transport properties discussed above, and the sensing of passing molecules regarding their types and conformations towards applications in DNA/RNA sequencing etc. Together with theory and modeling studies based on thermodynamics and statistical mechanics, atomic level molecular simulations and *ab-initio* modeling tools are expected to provide crucial information for the dynamics, process, and electronic and sensing properties of the CNT channel systems.

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Appendix

One-variable Fokker–Planck equation is expressed as²³:

$$\frac{\partial W(x, t)}{\partial t} = L_{\text{FP}} W(x, t), \quad (\text{A.1})$$

where $W(x, t)$ is the probability function. The Laplace operator L_{FP} is defined as,

$$L_{\text{FP}} = -\frac{\partial}{\partial x} D^{(1)}(x) + \frac{\partial^2}{\partial x^2} D^{(2)}(x). \quad (\text{A.2})$$

$D^{(1)}(x)$ and $D^{(2)}(x)$ are the drift and diffusion coefficients. The operator L_{FP} may be rewritten as the following, through a general potential function $\Phi(x)$:

$$L_{\text{FP}} = \frac{\partial}{\partial x} \left[D^{(2)}(x) e^{-\Phi(x)} \frac{\partial}{\partial x} e^{\Phi(x)} \right], \quad (\text{A.3.1})$$

$$\Phi(x) = \ln D^{(2)}(x) - \int_x \frac{D^{(1)}(x)}{D^{(2)}(x)} dx. \quad (\text{A.3.2})$$

For a one-dimensional Brownian particle, the drift and diffusion coefficients are written as:

$$D^{(1)}(x) = \frac{F(x)}{m\gamma(x)} = -\frac{\tilde{f}'(x)}{m\gamma(x)}, \quad (\text{A.4.1})$$

$$D^{(2)}(x) = \frac{\mu_{\text{B}}T}{m\gamma(x)}, \quad (\text{A.4.2})$$

where $\tilde{f}(x)$ is a general function for potential. With Eqs. (A.4.1) and (A.4.2), Eq. (A.3.2) is rewritten as:

$$\Phi(x) = \ln D^{(2)}(x) + \frac{\tilde{f}(x)}{k_{\text{B}}T} + \text{const.} \quad (\text{A.5})$$

Taking Eq. (A.5) into Eq. (A.3.1), the operator L_{FP} is rewritten as:

$$L_{\text{FP}} = \frac{\partial}{\partial x} \left[e^{-\tilde{f}(x)/k_{\text{B}}T} \frac{\partial}{\partial x} D^{(2)}(x) e^{\tilde{f}(x)/k_{\text{B}}T} \right] \quad (\text{A.6})$$

The corresponding mean first translocation time τ^{23} thus is expressed as:

$$\tau = \int_x e^{\tilde{f}(x)/k_{\text{B}}T} dx \int_{x'} \frac{1}{D(x')} e^{-\tilde{f}(x')/k_{\text{B}}T} dx'. \quad (\text{A.7})$$

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